[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY (No. 510) and of VASSAR COLLEGE]

FACTORS INFLUENCING THE ACCURACY OF MEASUREMENTS OF THE ELECTRICAL CONDUCTANCE OF LIQUIDS AND SOLUTIONS. II¹

A DISCUSSION OF THE BRIDGE ASSEMBLY FOR THE MEASUREMENT OF ELECTRICAL CONDUCTANCE WITH PARTICULAR REFERENCE TO THE VREELAND OSCILLATOR AS A SOURCE OF CURRENT OF CONSTANT FREQUENCY

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Introduction

The present status of our knowledge of methods for measuring the electrolytic conductance of solutions and liquids is such that it is quite necessary for a conscientious investigator, who wishes to make even a small number of determinations with any degree of precision, to have at his disposal a generous supply of both time and equipment. One reason for this state of affairs is that since the work of Kohlrausch² enough improvements in apparatus have been made and sources of error discovered to disturb the complacency of investigators as to the accuracy of results possible with the apparatus then used, but not enough to give them any confidence in the results obtainable with the newer assemblies now recommended since, in every instance, either for lack of time or equipment, workers in this field have had to abandon the problem after the publication of a few papers. Washburn³ made some noteworthy improvements in the bridge assembly as a whole but was obliged to give up the work before its completion. Taylor and Acree⁴ also attacked the problem as a whole and from another point of view, but it is ten years since their set of papers was published. Aside from these more extensive investigations, there have been isolated publications on more specific parts of the general problem. Curtis and Grover⁵

¹ A preceding paper, to which reference will be made as Part I, was published by us [THIS JOURNAL, **45**, 1692 (1923)] under the title "The Design and use of Conductance Cells for Non-Aqueous Solutions." As the general scope of the work has been broadened to include a study of the cause, magnitude, correction and possible elimination of the errors affecting not only the precision of relative results, but finally the absolute accuracy of the values for the electrical conductance of all types of liquids and solutions, the series is continued under the changed title given above.

² See Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," B. G. Teubner, Leipzig, 1898, and the references given there.

^a Washburn and Bell, THIS JOURNAL, **35**, 177 (1913). Washburn and Parker, *ibid.*, **39**, 235 (1917). Washburn, *ibid.*, **38**, 2431 (1916).

⁴ Taylor and Acree, (a) *ibid.*, **38**, 2396; (b) 2403; (c) 2415 (1916), and references given there.

⁵ Curtis and Grover, Bur. Standards Bull., Vol. 8, No. 3 (1911).

published a paper on resistance coils which has resulted in the fairly general use of Curtis coils for resistances over 1000 ohms. Schlesinger and Reed⁶ have pointed out some likely errors. Hibbard and Chapman⁷ have made a general résumé of the method in an attempt to find a simplified apparatus for botanists. Percy⁸ in surveying the work done up to 1922 makes a distinction between the resistance of the solution alone and of the solution with the electrode effects. Kraus and Parker⁹ have discovered some of the errors current in the determination of cell constants, and Parker and Parker¹⁰ have made a redetermination of the specific conductance of 0.1 N potassium chloride solutions. We, ourselves,¹¹ have pointed out some special precautions which must be taken when nonplatinized or dried cells are used. Aside from these researches, which in most cases are based on the Kohlrausch method of using alternating current, we have a number of isolated researches dealing with the use for conductance measurements of special methods such as the direct current method of Eastman.12

Nevertheless the determination of electrical conductivity is one of the most important, generally applicable and, once the apparatus is installed, quickly determined measurements we have. Its application to botanical, physiological, and industrial problems, as well as its application to the theory of aqueous and non-aqueous solutions and to the problem of fused salts is well known. Conductance data abound, notwithstanding the fact that we have no adequate method for what should be a very simple determination. There are practically as many equations relating conductance to other properties of a solution as there are investigators of conductance, and yet the most definite thing we can say about the accuracy of the results in the literature is that very few of them can have, for one reason or another, as much as a precision of 0.1%. What the absolute accuracy can be in view of the fact that practically all values are based upon some other value used as a standard had best be left unpredicted!

The difficulties involved in the absolute measurement of the conductance of solutions and liquids by the Kohlrausch alternating current method may be grouped into three classes; the first comprises those difficulties attendant upon the measurement of the resistance of a metallic conductor in a Wheatstone bridge circuit with an alternating current of definite frequency as the source of current; the second includes those difficulties peculiar to the

⁶ Schlesinger and Reed, THIS JOURNAL, 41, 1727 (1919).

⁷ Hibbard and Chapman, Michigan Agr. Coll. Expt. Sta. Tech. Bull., 23 (1915).

⁸ Percy, Inaugural Dissertation, Basel, 1922.

⁹ (a) Kraus and Parker, This Journal, 44, 2422 (1922). (b) Parker, *ibid.*, 45, 1366 (1923).

¹⁰ Parker and Parker, *ibid.*, **46**, 312 (1924).

¹¹ Morgan and Lammert, (a) *ibid.*, **45**, 1692 (1923); (b) **46**, 1117 (1924).

¹² Eastman, *ibid.*, **42**, 1648 (1920).

measurement of the relative resistance of the solutions and liquids themselves, which is to say those errors inherent in the conductance cell; and the third embraces all of those difficulties arising in the absolute measurement of the specific conductance of a standard solution. The first part of the problem has been worked out with greater success than the second; the situation at present is that whereas, with good judgment as to the selection and use of apparatus, the resistance of metallic conductors can be measured with an absolute accuracy approaching 0.001%, the absolute accuracy of the values for the resistance of electrolytes is unknown. In the first case, there is always the possibility of checking up the results against direct current values, while in the second case we have neither an adequate design for a cell with which consistent relative results can be obtained throughout all ranges of resistance, nor a standard solution, the infallibility of whose resistance is assured, since all values for the so-called standard solutions have been obtained either with an inferior bridge assembly or with cells, the design of which leads us personally to be pessimistic as to the value of the results.

It is our object, therefore, to make an experimental review of the instruments now recommended for alternating current work, in order to determine in the first place the limit of precision of each part of the bridge circuit as assembled for measuring a metallic conductor; second, to develop further^{11a} the technique of using the conductance cell and if necessary the design so that the limit of precision of the cell and its contents will be not less than the rest of the assembly; and third, after we know more of the so-called "electrode effects" and the magnitude and correction of the errors dependent upon them, to determine the absolute specific conductance of some liquid suitable as a standard. In this paper we are presenting some experimental details which, it is hoped, will bring together much that is useful to those working in the field and for the lack of which the present investigators wasted much time. Furthermore, it would seem wise to define at the outset just what is the precision of the various instruments, since among workers there is great divergence, dependent upon the uses to which the results are put and upon the attitude of the investigator, as to what constitutes precision in conductance measurements.

Experimental Part

Source of Current; Type A Vreeland Oscillator.—In the course of an investigation to develop methods for conductance measurements with an accuracy of 0.001%, Taylor and Acree^{4a} considered the various sources of alternating current and came to the conclusion that the various types of Vreeland oscillators were by far the best suited to conductance work. In the first place, they give the pure sine wave necessary for the prevention of unsymmetrical polarization at the electrodes and for the elimination of

the influence of harmonics and in the second place they were found to give sources of current of the most constant frequency, which frequency could be changed at will by changing the capacitance in the circuit. Of the induction coil, used so generally until recently, they report that it does not give an alternating but a pulsating current, with a large number of overtones and inconstant frequency and that the range of frequencies possible is small, while of the various types of motor generators they say that either a pure sine wave is possible only when the output is purified by inductance and capacitance in the circuit, or that the frequency is inconstant and not easily regulated.

Our experience corroborates Taylor and Acree's, in that we have found that it was necessary to give considerably more attention to the motor generator than to the Vreeland oscillator in order to obtain the very short range of complete silence in the telephone possible with the latter and, furthermore, that the special regulating device attached to give a constant frequency was continually out of order. Much to our amazement, however, we found these authors too optimistic about the constancy of the frequency of the oscillator under all conditions, which fact led us to make a systematic study of the laboratory Type A Vreeland oscillator in order to determine to what extent the frequency remains constant under varying conditions.

Whereas Taylor and Acree state that the frequency can be "kept constant for weeks to within 0.10%." Table I shows the typical action of our Type A oscillator during a day's run; in the first column is given the time in hours during which the oscillator has been operating; in the second column, the capacitance setting necessary to maintain the frequency at 1024 oscillations per second as tested by a standard tuning fork giving that

		SECON	DARY AND	INPUT IN PI	RIMARY		
Time, hours	Capacitance in primary circuit Microfarads	Frequency with constant initial capacitance ~	Temp. in condenser chamber, °C.	Time, hours	Capacitance in primary circuit Microfarads	Frequency with constant initial capacitance ~	Temp. in condenser chamber °C.
0.00	3.82	1024	28	3.25	3.89	1015	33
.25	3.835	1022	••	3.50	3.89	1015	32,3
. 50	3.84	1021		3.75	3.89	1015	32.6
.75	3.84	1021		4.00	3.895	1015	32.6
1.00	3.845	1021	30	4.25	3.895	1015	32.6
1,25	3.85	1020	30	4.50	3.90	1014	33.0
1.50	3.855	1020	30	7.25	3.90	1014	33.9
1.75	3.86	1019	31	9.00	3.90	1014	36
2.00	3.87	1017	32,5	10.00	3.90	1014	34.6
2.25	3.88	1016	32	11.00	3,90	1014	37
2.50	3.88	1016	32	12.00	3.90	1014	35
2.75	3,885	1016	32.5	13.00	3.90	1014	33.6
3.00	3.89	1015	32.6				

TABLE I

DATA Showing the Variation of Frequency of the Type A Vreeland Oscillator WITH THE TIME OF OPERATION-FREQUENCY 1024 ~--CONSTANT LOAD ON

number of vibrations per second; in the third column, the frequency which the oscillator would furnish at any one time had the capacitance in the oscillating circuit been kept at the same initial value; and in the fourth column, the temperature of the air surrounding the condensers.

The values in column three were calculated from the equation, used to express in such a circuit, the relation of the frequency to the capacitance and inductance, namely: $f = A \sqrt{1/C}$, where f is the frequency, C the capacitance, A a constant equal to $(1/2\pi\sqrt{L})$ and L the inductance in the circuit. The percentage change in frequency at constant capacitance equivalent to any percentage change in capacitance necessary for a constant frequency can be calculated from an equation obtained by the wellknown manner of differentiating the functional relationship, relating the two and dividing this by the original equation. Differentiating f = $AC^{-1/2}$, we get $df = -\frac{1}{2}AC^{3/2}dC$ and dividing by the original equation we have $(df/f) = -\frac{1}{2}(dC/C)$. That is, the percentage change in capacitance (dC/C) necessary to maintain a constant frequency multiplied by one-half gives, in the opposite direction, the percentage change in frequency (df/f) at a constant setting for the capacitance. The intermediate equation is included at this point to show that the fractional or percentage change gives a simpler relationship than the absolute changes df and dC.

From the data in Table I, it is evident that the frequency of the alternating current furnished changes rapidly at first but finally becomes constant after a run of about four and a half hours; the total change in frequency, that is, from $1024 \sim to 1014 \sim$, is about 1.0% instead of remaining constant to within 0.1% as stated by Taylor and Acree. It is of course, possible that the difference between their results and ours might have been due to a difference in a number of experimental conditions. In the first place these investigators may have made their observations after the oscillator had been running for some time and had come to a constant value; their statement "weeks at a time" rather implies this, whereas the more occasional investigator would be likely in the interests of economy to start the oscillator just before using.

Another possibility which it has occurred to us, might account for this difference is that our oscillator, being enclosed in a metal house for protection to the oscillator against dust and for protection to the bridge assembly against stray electrical field from the oscillator, was operating at a higher temperature than usual. Accordingly, holes were bored in the metal sheathed table supporting the instrument, a large electric fan other than the one provided for the oscillator was run in a horizontal position beneath it, and all the doors of the house opened. The differences in temperature of the chamber immediately surrounding the condensers are recorded in the fourth column. Although by opening and closing the windows of the room we were able to raise and lower the temperature in the compartment in which the condensers are situated 4° , nevertheless, once the frequency had become constant a considerable change in temperature of the atmosphere surrounding the oscillator had no effect. If, however, the small fan built into the oscillator does not function properly to cool the lamp, the instrument will no longer oscillate. Further runs were made removing the house entirely, but in so far as we were able to determine, provided the temperature of the lamp was kept sufficiently low to operate at all, any such changes in the outside temperature had little effect on the constancy of the frequency.¹³

Moreover, further runs indicated that this behavior of the oscillator was not affected by a change in the number of turns of wire in the secondary, by a change in the load on the secondary, nor by the angle of coupling of the secondary. Tests were made by turning in any number of the nine steps into which the secondary coil is divided, other conditions remaining the same, but there was no difference in the way in which the frequency changed: the same statement was true whether the oscillator was operated on open circuit, with telephones having a very different impedance connected directly across the secondary, or with the bridge assembly connected across the secondary in the usual way and the resistances varied through a large range. When the secondary was moved too close to the primary coils, as would be expected, the frequency, for any one capacitance setting, changed rapidly; within a certain range, however, no change was apparent when the secondary was moved to or from the lamp. The large mass of data collected to substantiate the statements made in this paragraph are omitted in the interests of economy of space, since the results for the most part were negative in nature.

It would seem, therefore, that the cause of the change in frequency lies in changes in the oscillating circuit produced by the oscillator in its operation. Although the makers¹⁴ state that "inductance coils and condensers are known to have very low temperature coefficients," nevertheless, Grover¹⁵ has shown that condensers may have temperature coefficients of considerable magnitude. It is possible, too, that the temperature coefficient of inductance is sufficient to account for some of the change, although the writers are not aware of any systematic published work on this subject, which would be applicable to the problem in hand.

The nature of the connections is such that the current flows through those

¹⁸ The temperature of the room did, however, seem to determine the initial capacitance at which the oscillator would operate to give a definite frequency, for it was observed that on cold mornings it took less capacitance than if the oscillator were started later in the day. After it had operated for a very short time, however, it resumed in such a case its usual setting and rate of increase of capacitance.

¹⁵ Grover, Bur. Standards Bull., 7, 495 (1911).

¹⁴ Leeds and Northrup, Catalog No. 10, p. 42.

condensers covered by the metal plate whenever the lamp is in operation; this is true whether the switch connecting the condensers to the primary circuit is closed or not, whereas the primary coils are not in the circuit when the switch is open and the lamp burning but not oscillating. Data, presented in Table II, were collected to determine whether the change was the greater in the inductance or in the capacitance. This was done by measuring the capacitance necessary to maintain the frequency constant at

TABLE II	
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DATA TO DETERMINE WHETHER THE CAUSE OF THE CHANGE IN FREQUENCY OF A TYPE A VREELAND OSCILLATOR IS DUE TO A CHANGE IN THE INDUCTANCE OR CAPACITANCE OF THE PRIMARY RESONATING CIRCUIT

Capacitance reading necessary to maintain a constant frequency of 1000 \sim

Time of operation of oscillator Hours	Condensers needed and primary coils in circuit Microfarads	Condensers needed in circuit but primary coils switched out except during readings Microfarads	Primary coils out and condensers in circuit reduced to minimum of 0.1 mf. except during readings Microfarads
0.00	3.90	3.91	3.89
.25	3.91	3.91	3.90
.50	3.91	3.91	3.90
.75		3.91	3.90
1.00	3.93	3.91	3.90
1.25	3,935	3.915	
1.50	3.94	3.92	3.905
1.75	3.95	3.93	••
2.00	3.955	• •	3.91
2.25		3.94	••
2.50	3.965	3.95	3.92
2.75		3.955	••
3.00	3.97	3.96	3.93
3.25	• •	••	••
3.50	3.97	••	3.94
3.75	••	• •	••
4.00	••	••	••
4.25	••	3.965	••
4.50	• •	3.97	••
4.75	3.97	3.97	••
5.00	••	••	3.96
5.25	••	3.97	••
5.50	3.97	••	• •
5.75	••	3.97	•••
6.00	3.97	• •	3.96
6.25	••	3.97	
6.50	3.975	••	3.96
6.75		3.97	
7.00	3.98		3.96
7.25	••	3.97	
7.50	••	••	3.90
7.75		••	
8.00	••		3.90

1000 cycles over a number of hours; first, when the condensers necessary at the start and the primary coils were kept in the resonating circuit (Col. 2); second, by making a similar run when the condensers were kept in the circuit but the primary coils were not (Col. 3); and third, when the primary coils were not in circuit and all condensers, except the 0.1 microfarad, which could not be eliminated, removed by turning the plate dials to the minimum setting possible except during readings (Col. 4).

From these data, it is evident that while the change in the value of the condensers, which takes place when a current is passed through them, is not responsible for *all* of the change in frequency with time of operation, since the change is different when the primary coils are in circuit (Col. 2)



Fig. 1.—Curve showing the effect of changes in capacitance and inductance produced by heating effects of current on the frequency of Type A Vreeland oscillator. *I*—Capacitance and inductance in primary circuit during operation. *II*—Capacitance in primary circuit during time of operation. *III*—Capacitance in circuit during time of operation; reduced to 0.1 mf.

than when they are not (Col. 3), nevertheless it is somewhat responsible as shown by the fact that the change is again smaller in effect when the condensers in the circuit are reduced to a minimum except during the time of measurement (Col. 4). These points are the more strikingly shown when the curves (Fig. 1) plotted from the data in Table II are examined. Curve I shows that when we have the effect of changing inductance superimposed upon changing capacitance, the frequency obtained changes rapidly from the first (or as we have measured it the nominal value of the capacitance necessary to keep the frequency constant has changed) and finally tends to become constant at a higher value, however, than under the conditions prevalent when Curves II and III were obtained. The greatest difference in the effects of the three different conditions imposed lies in the induction period, for under all conditions the frequency tends to become constant though at a somewhat different value, probably at that point where the heating effect and the radiation effect are in equilibrium or where the temperature coefficient of the condenser changes in value. The irregularities in the curves are of no importance, since the readings were made only to the nearest 0.005 microfarad, no closer account being taken of the relative length of the beats. Such irregularities would always occur in any change-time curve taken under the conditions of II or III, for there must of necessity be some time when readings are being taken during which the conditions are those under which Curve I was obtained; Point a of Curve II, for instance, is considerably below the general curve, an hour and a quarter having elapsed between the time of the previous reading and this one.

From these results, therefore, the situation seems to be this. The condensers and inductance used in the primary resonating circuit change their values, because of the heating effect of the current, the value of the condenser becoming less than the original value, with the result that more condensers need to be thrown into the circuit to keep the frequency constant, and the value of the inductance becoming smaller than its original value with the result that more capacitance must be thrown in, to counteract this effect and keep the frequency constant. The correction of this defect in the oscillator is one for the maker to assume. Grover¹⁵ states that the changes of capacitance with changes of temperature are much larger for paper condensers than for mica condensers, and that for paper condensers the temperature coefficient is in some cases negative and nearly constant, in some cases positive and rapidly increasing with the temperature, and in other cases the temperature coefficient is negative at lower temperatures and tends to become positive with increasing temperature. Some suitable condenser or combination of condenser and wire for inductance must be obtained which will have either no temperature coefficient or a constant temperature coefficient upon which sufficient reliance can be placed as to reproducibility to enable the investigator to obtain an equation general for all oscillators of the same type, or to have the assurance that the initial frequency given by the oscillator will be maintained over a period of time. However, until the makers supply such instruments with some sort of guarantee of test each investigator will have to determine for himself, whenever an accurate knowledge of the frequency is requisite, the conditions under which the oscillator can be used. This involves the use of very accurate tuning forks which are expensive. From results obtained in these Laboratories, it would seem that further developments in the field of electrolytic conductance must be in the direction of developing formulas relating the observed resistance of any one frequency and the real resistance; some work has already been done in this direction by Taylor

and Acree¹⁶ and by Haworth¹⁷ and consequently we cannot emphasize too much the need for a source of current of precisely constant frequency, which frequency can be varied at will. In principle, the Vreeland oscillator supplies such a source; in practice, some precautions must be taken in its use at the present time.

One other point, which we have considered, that may be of use to investigators lacking a supply of tuning forks, is the precision with which the formula $f = A \sqrt{1/C}$ will hold, provided we consider that the total capacitance C necessary to maintain a constant frequency f varies rather than, what is apparently true, that the total capacitance C does not vary but the number of condensers, whose real value had changed to a value below the nominal value, changed; in such a case A would of course vary for every new value of C substituted, f remaining constant. In this way, an investigator having only one tuning fork could calibrate the frequency of the current for one frequency to be used for measurement and, before sufficient time had elapsed, use the current at the other calculated frequency. As would be expected we found that by allowing the oscillator to operate at 1024 cycles we could check the calculated with the experimental values whenever the frequency desired required approximately the same or a smaller number of condensers; at the lower frequencies where the capacitance required was more than doubled, the experimental and the calculated results do not agree. Our suggestion would be, if a lower frequency is to be used, to run the oscillator most of the time with the maximum number of condensers required in the circuit and to change over to the higher frequencies only when needed. This would minimize if not entirely obviate the errors at the frequencies below 500.

TABLE III

FREQUENCY WITH THOSE CALCULATED FROM THE EQUATION $f = A\sqrt{1/C}$							
	C required for $1024 \sim$ Microfarads	$\begin{array}{l} \operatorname{Log} A \\ \operatorname{calcd. from} \\ f = 512 \sim \end{array}$	Calcd, C for 348 \sim from log A for 512 \sim Microfarads	Observed C for 348 ~ series connection Microfarads	Calcd. C for 500 ~ from log A for 512 ~ Microfarads	Observed C for 500 ~ series connection Microfarads	
	3.80	2.9992	8.23		3.985		
	3.81	2.9997	8.245	••	3.994	4.015	
	3.82	3.0003	8.27	8.08	4.005	4.015	
	3.83	3.0009	8.29		4.02	4.02	
	3.84	3.0014	8.31	8.105	4.025	4.025	
	3.85	3.0020	8.33	8.13	4.04	4.04	
	3.86	3.0026	8.36		4.05	4.05	
	3.87	3.0031	8.375	8.19	4.06	4.06	
	3.88	3.0037	8.40		4.07	4.07	
	3.89	3.0042	8.42	8.24	4.08	4.07	
	3.90	3.0048	8.44		4.09		

DATA COMPARING OBSERVED RESULTS FOR THE CAPACITANCE REQUIRED FOR A GIVEN FREQUENCY WITH THOSE CALCULATED FROM THE EQUATION $f = A\sqrt{1/C}$

¹⁸ Ref. 4(c) p. 2415.

¹⁷ Haworth, Trans. Faraday Soc., 16, 365 (1921).

In Table III are collected a few of the characteristic results, the field coils being connected in the circuit in series, and these are compared with those calculated from the value of C required for 1024 cycles, the field coils being connected in parallel.

Type D Vreeland Oscillator.—Three oscillators of this simpler type, intended by the makers to furnish 1000 cycles, but also provided with a switch to connect the condensers into the circuit so that 500 cycles can be obtained, were available for experiment. This type is much more temperamental in its operation than Type A oscillator, with the result that runs for any great length of time are difficult to obtain, particularly at 500 cycles. Following is the value of the lower frequency obtained on starting the three oscillators, which we shall call I, II and III: Oscillator I, 506; Oscillator II, 500; Oscillator III, 480.

By throwing the field coils in parallel we should get twice the value of these frequencies in place of the 1000~cycle expected. Quite apparently wherever, with precision, a definite frequency of either 500 or 1000 cycles is desired no dependence can be placed upon these oscillators, for the variation among the three tested is as high as 4%. This would be expected by anyone who had set up one of the oscillators of this type, for the lamp is furnished independently of the rest of the oscillator. Since the lamps vary somewhat in size and since the capacitance in the circuit and the framework carrying the primary coils are fixed, the distance of the primary coils from the lamp and hence the frequency are variable. It is our suggestion that some changes be made in the design of the oscillator in order that the distance of the primary coils from the lamp be more variable; in this way the frequency could easily be made that for which the oscillator supposedly is designed without the experimenter having to remodel the instrument entirely.

Oscillator III was run for several hours to determine how nearly constant the frequency furnished remained. The initial frequency was 480 cycles, the value then dropped to 476, in three hours rose to 480 again, and after six hours to 484 or 485, which value was maintained until the oscillator was shut off. The behavior of this oscillator is quite different from that of Type A in that there is an initial drop, but it can be explained when it is remembered that the primary coils of Type D oscillator are submerged in oil and surrounded by a coil through which cooling water passes and the condensers are on the top of the instrument, whereas in Type A the primaries are on top and air-cooled and the condensers are in an air chamber beneath the lamp.

Resistances.—The resistances most generally advocated for alternating current measurements are those designed by Curtis and Grover,⁵ their great advantage being that they vary little with a change in frequency. The makers supply them with an accuracy of 0.04%. Before furnishing a cer-

tificate, the Bureau of Standards requires the coils to have been aged for from four to six months before final calibration. It would seem, therefore, that after the first changes these coils could be relied upon for at least an accuracy of 0.04%. Such was not our experience, however. A resistance box of Curtis coils calibrated in October, 1921, which before calibration had been in our possession for over a year and was recalibrated in October, 1924, had changed in that time on an average about 0.5% on the reading of any one coil. Anyone, therefore, wishing to compare with precision results taken over any great length of time, should take the precaution to calibrate his coils to have them recalibrated from time to time.

Bridges.—A roller type Wheatstone bridge with a marble drum and metal top was used in the first part of this work, since we found, within the precision with which we were then working, no difference between our results taken with direct current and a galvanometer and with the alternating current from our Type D oscillator and a telephone. Taylor and Acree^{4c} had stated that errors as large as 1% might arise from the use of one of these bridges due to inductance from the coil and capacitance between the top and the coil. Parker^{9b} however, comparing his measurements with those made with direct current found no error in his results higher than 0.02%, over the greater portion of the bridge. Our experience would seem to corroborate the results of both of these investigations, for with the bridge mentioned above we were able to duplicate our results obtained with direct current to within 0.002% in the middle of the bridge when the extension coils were used, while with another bridge of the same type, made by the same company but supposedly a better bridge of later design and with a hard rubber or composition drum and cover, we were able to obtain practically any error we wished up to 1% by simply varying our position with respect to the apparatus. We were able to check our direct current reading with the latter bridge, only with the head of the operator in a most uncomfortable position and any slight movement of the position resulted in a shift in the value of the resistance and capacitance. That this was due to the bridge was finally discovered after all other parts of the assembly had been changed without effect; when, however, the bridges were interchanged, all other parts of the assembly being left in their identical positions, the source of our difficulty was located. That it was not due to body capacity was evident since the same effect was obtained when a stethoscope was attached to the telephones and then the telephones themselves were moved. The value depended upon the position of the head piece and connecting wires relative to the bridge and to the source of current.

Position of the Apparatus. Grounding and Shielding.—This heading is one of which a discussion is difficult in as much as the necessary precautions to be taken are quite likely to be different for different laboratories. The

Vreeland oscillator gives out considerable stray field, magnetic in nature, so that it cannot be cut off by a simple shielding. Moreover, the construction of the building seemed to play a considerable part in the difficulties encountered, for in one building we found it necessary to remove the apparatus a greater distance to cut out the effect than in another. It was our experience, however, that even with the substitution bridge where there could be none of the errors due to the construction of the bridge mentioned in the foregoing section the results for resistance and capacitance obtained with the alternating current only agreed with those obtained with the direct current when the apparatus was so placed that the operator could stand out of the field produced by the Vreeland oscillator. It is our advice for the investigator to place the apparatus as far distant in the building as is feasible and then, by means of a telephone sufficiently sensitive to pick up the field with the unattached wires, determine the direction of the reresidual field, finally placing the apparatus in such a position that the operator may stand or sit easily and comfortably in the direction of no field and consequently will hear no noise in the telephone except when the bridge is connected into the actual circuit and there is a current flowing due to the lack of balance of resistance or capacitance in the arms of the bridge network. A change from this direction of position will, unless the oscillator is far distant, produce a change in the readings of either resistance or capacitance or both. Errors as large as 1% or more can be introduced in this way.

The method of grounding which we have found most effective is the modified form of Wagner described by Taylor and Acree.^{4c} By this method each end of the bridge is grounded through a 1000-ohm resistance and the lead wires from the oscillator shielded and grounded. We cannot emphasize too much the need for a good ground in order to get a sharp minimum. With the set-up described there is probably nothing which so affects the sharpness of the minimum as the condition of the ground. Sometimes a water pipe can be used, but as the water pipes in the building are often part of its electrical circuit, a separate connection is desirable to the girder of the building or to the ground directly, where the geology of the locality is such that a deep ground is possible.

Something can often be accomplished by way of sharpening the minimum by shielding the apparatus—one part from another, with a metal shield which is grounded. Care must be taken, however, to see that no part of the wire used in the assembly is shielded and grounded in such a way that the insulated wire with its shield becomes a capacitance in addition to the resistance offered by the wire.¹⁸

¹⁸ Note added March 6: The editorial referee has called our attention to the fact that he has found it better to have the leads in the neighborhood of the bridge approach the bridge vertically, but we have not as yet been able to test the value of the suggestion experimentally.

Summary

1. A systematic study has been made of a Type A Vreeland oseilhator as a source of alternating-current of constant frequency: The frequency at 1000 cycles has been found to decrease during a day's time of operation under the conditions of use, to the amount of 1%, finally becoming constant. The magnitude of the change appears to be dependent upon a decrease in the value of the capacitance and inductance in the primary resonating circuit caused by the heating effect of the current and to be independent of the angle of coupling, relative position of the primary and secondary coils if not placed too closely, load on the secondary or, except for a slight dependence of the initial frequency supplied with a certain setting of capacitance, of the room temperature. Methods and suggestions are given for the use of the oscillator in its present form for precision work where an accurate knowledge of the value for the frequency is necessary.

2. Three Type D oscillators have been tested and found to differ, on starting, from their rated value of 500 cycles from 0 to 4%. This type of oscillator also changes in frequency with time of operation, the value decreasing at first, then increasing and finally becoming constant.

3. The Curtis type of resistance coils (1000 ohms) has been found to change in value over a period of three years by about 0.5% of the nominal value of each coil, the coils being at least a year old before the first calibration. For precision work, therefore, coils of this type must be recalibrated from time to time.

4. Two roller type Wheatstone bridges have been examined to determine whether this type could be used for precision work in place of the more expensive ratio coil substitution bridge. It was found that whereas the results obtained with one bridge agreed to within 0.002%, those obtained with the other differed from the results obtained with direct current by as much as 1.0%, the magnitude of the change depending upon the position of the operator. For precision work, therefore, it would seem necessary to test out each bridge before any reliance could be placed upon the results.

5. Methods of shielding and grounding the assembly are discussed?

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